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Synthesis of Main Group Polycations in Molten and Pseudo-Molten $GaBr_3$ Media

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The prospects of synthesizing polycationic species using $GaBr_3$ in benzene solution at room temperature have been investigated. The salts $Bi_8[GaBr_4]_2$, $Sb_8[GaBr_4]_2$ and $Te_4[Ga_2Br_7]_2$ have been isolated and characterized. The first two compounds are isotypic with $Sb_8[GaCl_4]_2$, crystallize in the space group $Pna2_1$, and feature square *anti*-prismatic E_8^{2+} polycations (E = Sb, Bi). Unit-cell parameters for $Bi_8[GaBr_4]_2$ are a = 18.3014(10) Å, b = 10.3391(6) Å and c = 13.5763(7) Å, and for $Sb_8[GaBr_4]_2$; a = 18.096(2) Å, b = 10.1572(9) Å and c = 13.2168(10) Å. $Te_4[Ga_2Br_7]_2$ crystallizes in the space group $P2_1/c$ with a = 10.1600(9) Å, b = 10.8314(9) Å, c = 13.8922(10) Å and β = 99.182(7)°, and features a square-planar Te_4^{2+} polycation. The compound $Bi_5[GaBr_4]_3$ has been synthesized from molten $GaBr_3$ and characterized by using powder diffractometry in space group $Fm\text{-}3c$; a = 17.6263(8) Å. The structure model for this compound suggests the included Bi_5^{3+} cations to be practically freely oriented within its cavities in the solid phase.

Introduction

Homopolyatomic ions of the main-group elements have for a long time been an area of many studies and discussions, resulting in a large number of publications.[1] Species such as Cd_2^{2+}, Bi_8^{2+}, Bi_9^{5+}, Se_8^{2+}, Te_4^{2+}, I_3^+ etc. have been synthesized employing several different routes, for instance using molten salts or superacidic media.[2] Recently, in a series of papers we have illustrated the possibility to obtain polycations from $GaCl_3$–benzene solutions.[3–6] This method is based on the extraordinarily high solubility of $GaCl_3$ in benzene, which renders a pseudo-melt behavior to the saturated solution.[7] Thus, it has been possible to repeat, at room temperature, several of the reactions previously performed in molten $AlCl_3$. The major advantage of performing reactions at low temperatures is that it allows easier study of reactants and products in solution, using for instance spectroscopy. The method also offers some possibility to influence processes like crystal growth, as recently demonstrated by the successful isolation of the previously unknown $Sb_8[GaCl_4]_2$.[5]

Unfortunately, there are only very few other Lewis acids known with a propensity comparable to $GaCl_3$ for dissolution in benzene or other non-polar solvents. However, there is one obvious alternative – $GaBr_3$. The properties of $GaBr_3$ are similar to those of $GaCl_3$; the same structure in the solid phase and also a very high solubility in arenes, albeit not as high as its chloride congener. It can be noted that only very few *bromo*-aluminate/gallate/indate salts containing main-group polycations have been reported in literature – $Te_4[AlBr_4]_2$[8] and $Bi_8[InBr_4]_2$.[9] It is not known to us if the brevity of this list, in comparison to the record of chloroaluminate structures, is due to unforeseen complications in their syntheses or if it just reflects the small number of synthetic attempts made. The main goal of this investigation is to extend the knowledge on main-group polycation chemistry, employing a $GaBr_3$–benzene system as reaction medium because; (i) it is chemically closely related to the $GaCl_3$–benzene system, known to be successful; (ii) only a few reports have been made about the isolation of crystalline compounds from ternary M–Al/Ga/In–Br systems, and; (iii) it allows the possibility to affect polycation chemistry and thereby a possibility to isolate new polycations in the liquid or solid state.

The following sections describe observations made regarding the synthesis of a selection of main-group polycations in $GaBr_3$–benzene media. Some experiments have also been performed in molten Bi–$BiBr_3$–$GaBr_3$ systems.

Results and Discussion

The syntheses performed in this work followed the general procedures developed for the analogous $GaCl_3$–benzene system, which have been well described in earlier papers.[3–6] The solubility of gallium tribromide in benzene at ambient

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conditions is somewhat lower than that of gallium trichloride, estimated within this work to be ca. 8–9 mol%. In order to confirm the nature of $GaBr_3$ when dissolved in benzene, Raman spectra were recorded, see Figure 1, and compared with known spectra of Ga_2Br_6.[10] This evaluation verifies that gallium tribromide predominantly exists as dimeric units in benzene solution.

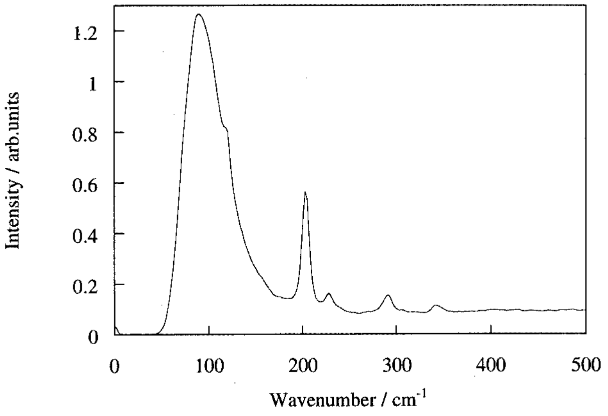

Figure 1. The Raman spectrum of $GaBr_3$ in benzene solution.

$Bi–GaBr_3$–Benzene Systems

Most of our work considering $GaBr_3$–benzene systems has been devoted to attempts to isolate bismuth polycations. First, the oxidation of bismuth metal by $GaBr_3$ in benzene solution was analyzed. In contrast to the reaction between bismuth and $GaCl_3$ in benzene, for which a red color can be noticed after a few hours, no coloration or other visible changes are observed in the $Bi–GaBr_3$–benzene case. However, after a few days it was noticed that the bismuth metal surface had lost it luster due to the formation of a black substance. By repeatedly exposing the crude product to fresh $GaBr_3$-benzene solutions, a sufficient amount of this black phase was obtained.

The final product was characterized by using powder X-ray diffraction. Although bismuth metal constituted a major impurity, it was possible to obtain the unit cell parameters for the black phase from the indexed reflections. The compound crystallizes in space group $Pna2_1$, a = 18.3014(10), b = 10.3391(6), c = 13.5763 Å. It was noted that this cell is very similar to the cells of $Sb_8[GaCl_4]_2$ and $Sb_8[GaBr_4]_2$ (see below), and the black phase was assumed to be $Bi_8[GaBr_4]_2$ (**1**). The coordinates of $Sb_8[GaBr_4]_2$ were used as starting coordinates in the Rietveld refinement of **1**. From the difference pattern it was concluded that the sample contained a third phase, the positions of the unassigned reflections matched known positions of $GaBr_3$, and this phase was added to the refinement.

The structure of **1** features a distorted square-antiprismatic Bi_8^{2+} cation and two tetrahedral $GaBr_4^-$ anions. The distortion of the cation is illustrated by the fact that the two Bi_4 squares are not parallel, see Figure 2. As a consequence, the variation in Bi–Bi distances is large, 2.88(2)–3.23(3) Å, see Table 1. In the discussion on $Sb_8[GaCl_4]_2$,[5] it was observed that for the antimony cluster the inter-square Sb–Sb distances are 3.3% longer than the intra-square distances, while the inter-square metal–metal distances in the case of $Bi_8[GaCl_4]_2$ are only 0.4% longer than the intra-square ones. The mean values for inter-square and intra-square Bi–Bi distances in **1** are 3.07(9) and 3.00(6) Å, respectively, giving a ratio of 1.023. This ratio is close to the one found for the Sb_8^{2+} cation, however, the distortion of the cation in **1** invites to some care in the interpretation.

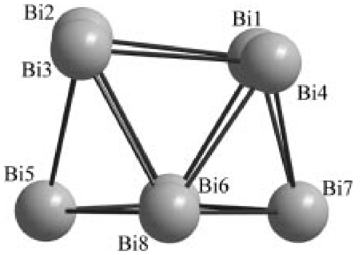

Figure 2. The Bi_8^{2+} cation of **1**. The two Bi_4 squares are not parallel to each other, consequently a large variation in Bi–Bi distances is observed.

Table 1. Bond lengths of **1**. Bismuth atom labels are given in Figure 2.

Atoms	Distance [Å]	Atoms	Distance [Å]
Intra-square bonds		*Inter-square bonds*	
Bi(1)–Bi(2)	2.95(2)	Bi(1)–Bi(6)	2.92(2)
Bi(1)–Bi(4)	3.03(3)	Bi(1)–Bi(7)	3.06(2)
Bi(2)–Bi(3)	2.97(3)	Bi(2)–Bi(5)	3.18(3)
Bi(3)–Bi(4)	3.14(4)	Bi(2)–Bi(6)	3.15(3)
Bi(5)–Bi(6)	2.95(3)	Bi(3)–Bi(5)	3.15(2)
Bi(5)–Bi(8)	2.94(3)	Bi(3)–Bi(8)	3.10(3)
Bi(6)–Bi(7)	3.04(3)	Bi(4)–Bi(7)	2.98(3)
Bi(7)–Bi(8)	2.98(3)	Bi(4)–Bi(8)	3.01(3)
Anion 1		*Anion 2*	
Ga(1)–Br(1)	2.35(4)	Ga(2)–Br(5)	2.33(4)
Ga(1)–Br(2)	2.37(4)	Ga(2)–Br(6)	2.33(5)
Ga(1)–Br(3)	2.32(4)	Ga(2)–Br(7)	2.35(4)
Ga(1)–Br(4)	2.36(4)	Ga(2)–Br(8)	2.36(4)

In our studies, it has been generally observed that the recording of Raman spectra is problematic for solid compounds containing bismuth polycations, probably due to heavy absorption. Therefore, no reliable Raman spectrum for **1** has been obtained.

If instead the reduction of $BiBr_3$ by Ga metal in $GaBr_3$–benzene is considered, the outcome is likewise problematic and different from the analogous reaction in the chloride system. The mixing of a solution containing $BiBr_3$ with one containing Ga^+ ions causes an immediate formation of a black precipitate, while the solution remains colorless. No subvalent bismuth species can be registered in the liquid phase by use of Raman spectroscopy. The black substance can be inspected by means of X-ray powder diffraction and has been found to be amorphous, most likely due to the instantaneous precipitation.

Obviously, the speed of precipitation has to be reduced in order to obtain proper crystals. By using a special set-up, allowing for a very slow speed of mixing, a small amount of tiny, black, bar-shaped crystals could be isolated. A unit cell determination for one of these crystals shows that they belong to the orthorhombic system with the unit cell parameters: a = 23.854(6) Å, b = 15.634(5) Å, c = 9.128(5) Å; hence in very good agreement with the unit cell parameters of Bi_6Br_7.[11] This is quite remarkable, as it is the first salt, isolated from this synthetic method, that not includes halidogallate anions. Furthermore, this implies that Bi_9^{5+} cations are likely to be present in the solution at very low concentrations, undetectable by spectroscopy. The reasons why bromogallate(III) anions are not incorporated into the crystallization product are not yet clear. One possible explanation may lie in the expected thermodynamic stability of Bi_6Br_7 in combination with weaker Lewis acidity of $GaBr_3$ with respect to $GaCl_3$.

The main conclusion drawn from the synthesis of bismuth polycations in $GaBr_3$–benzene media is that compounds containing polycations form; $Bi_8[GaBr_4]_2$ and Bi_6Br_7 have been isolated. However, although the reaction principles work, the solubility of the formed polycations in media containing bromogallates ions is very low, and the crystal growth is severely hampered with reduced crystal size as consequence.

Molten Bi–$GaBr_3$ and Bi–$GaBr_3$–$BiBr_3$ Systems

In order to obtain crystals of **1** of better quality, an attempt on the direct high-temperature oxidation of bismuth by gallium tribromide was made. However, no interaction between the components was observed even after a week of annealing at 350 °C. This clearly demonstrates the vital role of benzene in coordinating Ga^+ cations formed on the reduction of Ga^{III} in $GaBr_3$–benzene media.

Instead, symproportionation was employed; from a solid state synthesis, the starting materials having the ratio 4Bi:$BiBr_3$:4$GaBr_3$, a red-brown microcrystalline material could be obtained. The recorded powder X-ray diffractogram of this product shows strong similarities to that of the previously characterized cubic modification of $Bi_5[GaCl_4]_3$.[3] In analogy to that structure, the diffraction pattern was indexed as F-centered cubic with a = 17.6263(8) Å. The atomic coordinates for the chloride structure were taken as the initial model for full-profile Rietveld refinement. The atomic coordinates for this phase, cubic $Bi_5[GaBr_4]_3$ (**2**), are given in Table 2.

Both **2** and cubic $Bi_5[GaCl_4]_3$ are related to the rhombohedral form of $Bi_5[GaCl_4]_3$.[6,12] All these three compounds contain trigonal bipyramidal Bi_5^{3+} polycations and tetrahedral GaX_4^- anions as the structural units (see Figure 3). However, the difference for the cubic phases is that their description within the given crystal system implies a substantial degree of disorder. Eight Bi_5^{3+} units, occupying centers of octants in the cubic cell, may in the cubic $Bi_5[GaCl_4]_3$ have 4 different orientations parallel to the body diagonals of the cube. In **2**, the positions of Bi(2) are slightly off the body diagonals, resulting in 8 possible positions. In practice, it is hardly meaningful to discuss the polycations in terms of atomic positions, the number of possible positions, together with the relatively large displacement parameter, suggest that the Bi_5^{3+} polycations can be assumed to rotate freely in all direction within its cavities, defined by the positions of the tetrabromogallate anions. Therefore, it has also not been relevant to analyze any Bi–Bi distances of this cation. In contrast, the anions are found to be almost ordered, although a second bromine site, occupied by 6% of the bromine atoms, has been refined. The Ga–Br(1) distance is found to be 2.338(4) Å, in good agreement with the reported distance of the tetrabromogallate anion.

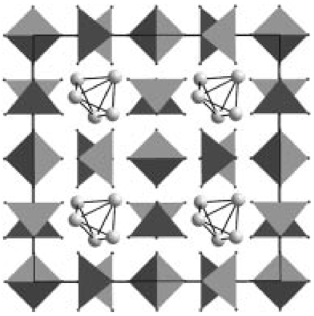

Figure 3. An idealized two-dimensional projection of the unit cell content of **2**. The Bi_5^{3+} polycations are displayed in one of all possible orientations and the Br(2) atoms have been omitted.

In the case of cubic $Bi_5[GaCl_4]_3$ it has already been concluded that no further information is added to the structure solution through the generation of single crystals.[6] One possible explanation may be that the cubic phase is a microtwinned modification of the rhombohedral one (still to be isolated in the case of $Bi_5[GaBr_4]_3$).

It can be noted that all the attempts to produce more bismuth-rich compounds from molten Bi–$BiBr_3$–$GaBr_3$ (e.g. $Bi_8[GaBr_4]_2$) resulted in the formation of **2** and some unreacted bismuth metal in the reaction container, i.e. no

Table 2. Refined fractional coordinates, isotropic temperature coefficients and occupancy factors for **2**.

Atom	Position	SOF	x/a	y/b	z/c	B_{iso} [Å]^2
Bi1	192j	0.070(3)	0.3068(10)	0.1591(10)	0.2609(12)	5.0(4)
Bi2	192j	0.123(3)	0.1632(7)	0.1777(10)	0.2005(6)	5.0(4)
Ga	24*c*	1	0	0	1/4	2.0(2)
Br1	96*i*	0.942(3)	0.3876(2)	0.3204(2)	0	2.8(1)
Br2	96*i*	0.058(3)	0.256(3)	0.162(4)	0	2.8(1)

other ternary cluster compound was obtained in this system through the molten salt route of synthesis.

Synthesis and Crystal Structure of $Sb_8[GaBr_4]_2$

Also the reactions of antimony in $GaBr_3$–benzene have been studied. In the case of antimony it has previously been noted that elemental antimony is not oxidized in $GaCl_3$–benzene, probably due to low solubility.[5,13] It is assumed that the same is true for the bromide case, hence only the reduction of $SbBr_3$ by Ga metal has been empolyed. From this route, a large amount of a black amorphous phase together with a few small orange crystals have been isolated. Single-crystal X-ray diffraction and Raman spectroscopy experiments have confirmed the orange crystals to be $Sb_8[GaBr_4]_2$ (**3**).

The structure of **3** is isotypic to the structure of **1**, described above, as well as the chloride analogue, $Sb_8[GaCl_4]_2$,[5] with an increase in unit cell volume of 8.6%. The structure features a Sb_8^{2+} polycation, the geometry being very close to square-antiprismatic (although the true molecular symmetry is C_1), and two crystallographically independent tetrabromogallate tetrahedra, see Figure 4. The Sb–Sb distances vary between 2.854(2) and 2.890(2) Å [mean: 2.871(11) Å] within the squares, while the inter-square distances vary between 2.940(2) and 2.987(2) Å [mean: 2.97(2) Å], see Table 3. Thus, the inter-square/intra-square distance ratio is found to be 1.035 (see discussion on the structure of **1**). This is in very good agreement with the distances of the cation found in the tetrachlorogallate structure. The Ga–Br distances are in the interval 2.299(3)–2.327(3) Å. Just as in the case of the chloride structure, there are some rather short cation–anion distances, the shortest being 3.552(2) Å.

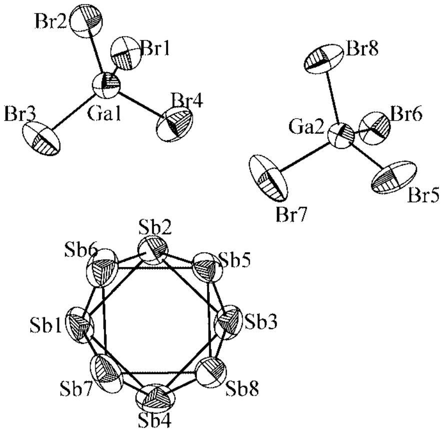

Figure 4. The atoms of the asymmetric unit of **3**. Thermal ellipsoids are drawn at the 70% probability level.

Raman spectroscopy on selected single crystals of **3** reveals signals at $\tilde{\nu}$ = 177 (s) and 209 (m) cm^{-1}. The first one corresponds to the strongest Raman peak of the Sb_8^{2+} polycation, shifted a few wavenumbers down with respect to the chloride structure, while the latter peak corresponds to the strong symmetrical stretch vibration mode of the $[GaBr_4]^-$ ion.[14]

Table 3. Bond lengths of **3**. Atom labels are given in Figure 4.

Atoms	Distance [Å]	Atoms	Distance [Å]
Intra-square bonds		*Inter-square bonds*	
Sb(1)–Sb(2)	2.864(2)	Sb(1)–Sb(6)	2.958(2)
Sb(1)–Sb(4)	2.880(2)	Sb(1)–Sb(7)	2.984(2)
Sb(2)–Sb(3)	2.861(2)	Sb(2)–Sb(5)	2.974(2)
Sb(3)–Sb(4)	2.890(2)	Sb(2)–Sb(6)	2.962(2)
Sb(5)–Sb(6)	2.878(2)	Sb(3)–Sb(5)	2.954(2)
Sb(5)–Sb(8)	2.861(2)	Sb(3)–Sb(8)	2.973(2)
Sb(6)–Sb(7)	2.880(2)	Sb(4)–Sb(7)	2.940(2)
Sb(7)–Sb(8)	2.854(2)	Sb(4)–Sb(8)	2.987(2)
Anion 1		*Anion 2*	
Ga(1)–Br(1)	2.327(3)	Ga(2)–Br(5)	2.303(2)
Ga(1)–Br(2)	2.318(3)	Ga(2)–Br(6)	2.312(2)
Ga(1)–Br(3)	2.301(3)	Ga(2)–Br(7)	2.296(3)
Ga(1)–Br(4)	2.320(3)	Ga(2)–Br(8)	2.310(2)

Neither X-ray diffractometry nor Raman spectroscopy proved to be useful in the characterization of the black precipitate, which is the major product of the reaction above. Energy-dispersive X-ray analysis (EDX) was performed on this compound in order to obtain some information of its contents. Unfortunately, the results of these measurments are ambiguous. The observed Ga:Br ratio (1:2) is unexpectedly low; not an uncomon result of elemental analyses in gallate systems. On the other hand, the observed Sb content tend to match the expected theoretical values. Based on the assumption that the Sb content is in good agreement also for this black product obtained from the reduction of $SbBr_3$, it can be conluded that the phase contains an antimony polycation and that it is likely to be a another polycation than Sb_8^{2+} (theoretical Sb content; 44%). Plausible compounds, based on the antimony content (ca. 24%), include $Sb_5[GaBr_4]_3$ (25%), $Sb_6[GaBr_4]_4$ (23%), $Sb_7[GaBr_4]_5$ (22%) and $Sb_8[GaBr_4]_4$ (29%).

Te–$GaBr_3$–Benzene

It has also proved feasible to synthesize polycations of elements from other groups than group 15 by using the benzene route. Recently, $Te_4[Ga_2Cl_7]_2$ was isolated from $GaCl_3$–benzene media,[15] and other ions may be attainable in the analogous bromide system. Therefore, a series of experiments were pursued, attempting to oxidize different elements to polycations in $GaBr_3$–benzene solution.

No reaction was detected in the case of cadmium, arsenic or selenium. However, in the case of tellurium, the solution becomes slightly green in color within a couple of hours after the addition of elemental tellurium. After a few days this color disappears, and instead small, black, block-shaped crystals are formed. Unfortunately, the crystals are too small to allow for even a unit cell determination and the Raman spectrum is ambiguous, showing only one band at 210 cm^{-1}, which could be attributed to different expected ions such as Te_4^{2+} or $GaBr_4^-$.[14,16]

Instead, reduction of $TeBr_4$ with Ga metal in $GaBr_3$–benzene is successful, and violet, plate-shaped crystals were obtained. Single-crystal diffraction confirms these crystals to contain $Te_4[Ga_2Br_7]_2$ (**4**), the formula analogue of the compound previously found in the chlorogallate case.[15] **4** is found to crystallize in the space group *P*2$_1$/*c*, just like the previously reported chlorogallate structure, however the unit cell parameters are different, with a much larger β-angle [99.182(7)°] in the case of **4**.

The structure of **4** features a square-planar Te_4^{2+} cation and staggered $[Ga_2Br_7]^-$ anions, see Figure 5. Selected bond lengths for **4** are given in Table 4. The Te–Te distances are 2.6702(14)–2.6720(14) Å, which compares well with other structures containing this cation.[1c] The distances between the gallium atoms and the terminal bromine atoms, 2.266(2)–2.331(2) Å, are in the normal range for Ga–Br bonds. Just as in $Te_4[Ga_2Cl_7]_2$ and $Te_4[Al_2Cl_7]_2$,[17] there are some rather short Te–X distances (X = Cl, Br), of which the shortest are found for bromides positioned in the plane of the cation, capping the edges of the square-planar cation. In this particular structure, the shortest Te–Br distance is 3.412(2) Å.

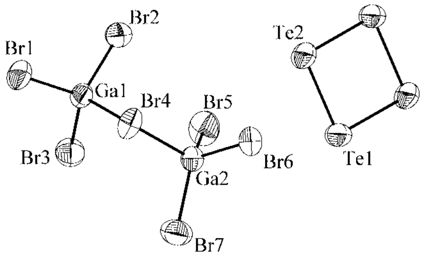

Figure 5. The atoms of the asymmetric unit of **4**. Thermal ellipsoids are drawn at the 70% probability level. Unlabelled Te atoms are related to Te(1) and Te(2) by the inversion operator (1 – *x*, 1 – *y*, –*z*).

Table 4. Bond lengths of **4**. Atom labels are given in Figure 5.

Atoms	Distance [Å]
Te(1)–Te(2)	2.6702(14)
Te(2)–Te(1)^i	2.6720(14)
Ga(1)–Br(1)	2.290(2)
Ga(1)–Br(2)	2.311(2)
Ga(1)–Br(3)	2.275(2)
Ga(1)–Br(4)	2.432(2)
Ga(2)–Br(4)	2.445(2)
Ga(2)–Br(5)	2.274(2)
Ga(2)–Br(6)	2.331(2)
Ga(2)–Br(7)	2.266(2)

In the Raman spectrum recorded from a single crystal of **4**, bands are observed at 419 (*m*), 314 (w), 250 (br) and 210 (s) cm^{-1}. The lowest band is attributable to the cation,[16] and the bands at 250 and 314 cm^{-1} to the anion.[18] The origin of the peak at 419 cm^{-1} is unknown, but a similar band was observed for $Te_4[Ga_2Cl_7]_2$, which in the report of that compound, was suggested to be attributed to the chlorogallate anion.[15] However, this may possibly be a common band of both structures, originating either from the cation or an impurity.

It can be concluded that the Te_4^{2+} cation has the highest solubility of the polycations formed in $GaBr_3$–benzene; a colored solution is retained at least for a couple of minutes when reducing $TeBr_4$ with Ga metal, instead of immediate precipitation as in the cases of $BiBr_3$/$SbBr_3$. Furthermore, a slight coloration of the solution can be observed also when elemental tellurium is put in $GaBr_3$–benzene, and small crystallites are formed spatially separated from the solid reactants, hence, transport via solution must occur.

Conclusions

Experimental attempts to synthesize polycations of different elements in $GaBr_3$–benzene solutions have been performed. For all experiments in such media, the problem of low solubility of the products formed represents a serious complication, lowering the quality of the crystalline materials obtained. Nevertheless, the compounds $Bi_8[GaBr_4]_2$, $Sb_8[GaBr_4]_2$ and $Te_4[Ga_2Br_7]_2$ have been isolated and their structures characterized, illustrating the similarity in chemistry between $GaCl_3$ and $GaBr_3$ in benzene media. Additionally, $Bi_5[GaBr_4]_3$ has been isolated from molten $GaBr_3$ and its structure has been partly characterized.

Experimental Section

Chemicals: Commercial Bi (Aldrich, 99.999%), Ga and In metals (both ALFA Chemicals, 99.9999%), bromine, $BiBr_3$ (Aldrich, 99.9%), $SbBr_3$ (Aldrich, 99.99%), $TeBr_4$ (Aldrich, anhydrous, 99.995%) and $GaBr_3$ (Aldrich, anhydrous, 99.999%) were used as purchased. For certain experiments $GaBr_3$ was synthesized from the elements according to a literature procedure.[19] Benzene (Merck, pro analysi grade) was distilled and stored over molecular sieves in a glovebox under a dry nitrogen atmosphere. Because of the high moisture sensitivity of the anhydrous metal halides used in this work, all operations were performed in a glovebox under dry nitrogen with less than 0.5 ppm H_2O.

Synthesis of 1: Bi metal powder (0.2 g, 1 mmol) was added to 0.7 g of a saturated $GaBr_3$/benzene solution in a standard NMR tube. No obvious signs of reaction, such as change of solution color, were observed, but after a few days it could be noticed that a black substance had formed on the surface of the metal. From X-ray powder diffraction the crude product was found to a mixture of bismuth metal and an unknown compound. In order to improve the purity of the unknown phase, the product was washed with pure benzene, dried, re-ground and added to a fresh $GaBr_3$/benzene solution. These steps were repeated several times until a satisfactory purity of the product was obtained.

Synthesis of Bi_6Br_7: Two solutions, In–$GaBr_3$–benzene and $BiBr_3$–$GaBr_3$–benzene, were prepared and added to two vessels connected by a bridge, an overturned U-shaped tube, filled with pure benzene.[20] The reactor was then sealed to prevent solvent evaporation. After a month, some crystallization was observed in the form of black bars at the bend of the bridge.

Synthesis of 2: A mixture with the ratio of 4Bi:$BiBr_3$:4$GaBr_3$ was heated to 350 °C in a evacuated and sealed standard 5 mm NMR tube for several days and then slowly cooled to room temperature. The excess of gallium tribromide was removed by sublimation at 150 °C under dynamic vacuum. The obtained product is a dark brown microcrystalline mass, brick red when powdered.

Synthesis of 3: $GaBr_3$ (0.30 g, 1.0 mmol) was dissolved in benzene (1.0 mL) and the solution was separated into two parts. $SbBr_3$ (0.035 g, 0.1 mmol) was added to one of the solutions and Ga metal (0.02 g, 0.3 mmol) to the other. After 24 hours, the two solutions were mixed. A black precipitate formed immediately while the solution remained colorless. When the product was studied under microscope, it was noticed that small crystals of **3** had formed as orange cylinders together with the amorphous, black, main product.

Synthesis of 4: $GaBr_3$ (0.30 g, 1.0 mmol) was dissolved in benzene (1.0 mL) and the solution was separated in two parts. $TeBr_4$ (0.05 g, 0.1 mmol) was added to one solution and Ga metal (0.02 g, 0.3 mmol) to the other. After 24 hours, the two solutions were mixed, and a very darkly green solution formed. After a few minutes a dark precipitate formed and the solution became clear. Crystals of **4** were found as violet plates.

Raman Spectroscopy: Raman spectra from solutions were recorded using Bruker IFS-66/FRA-106 and Bio-Rad FT-Raman spectrometers equipped with a low power Nd:YAG laser (1064 nm) and solid state Ge detector cooled by liquid nitrogen. A resolution of 4 cm^{-1} was used in all measurements. Spectra from single crystals, mounted in standard melting point tubes, were recorded using a Renishaw System 1000 spectrometer, equipped with a DMLM Leica microscope and a 25-mW He-Ne laser (633 nm).

Elemental Analysis: Energy dispersive X-ray Analysis was performed on the amorphous black product formed contemporarily with the formation of **3**, using a JEOL JSM-820 scanning electron microscope. Totally 16 points at three different areas of a sample of the amorphous compound was measured. The observed average contents were (standard deviation in parenthesis): Sb, 24 (3) atom-%; Ga, 26 (3) atom-%; Br, 50 (1) atom-%.

Powder X-ray Diffraction: The powder diffraction data were collected using an INEL powder diffractometer, equipped with CPS-120 position-sensitive detector. The detector was calibrated with a $Pb[NO_3]_2$ standard and the diffraction pattern re-calculated into an equal-step pattern using a cubic-spline function. Standard 0.3 or 0.5 mm Lindemann capillaries were used as sample containers. The samples were kept spinning during the data collection. The Rietveld analyses of the powder diffraction data of **1** and **2** were performed using a local version of the LHPM1 program,[21] and employed pseudo-Voight profile functions, limited to 18 half-widths, with five-peak asymmetry correction, a Lorentzian component $\gamma = \gamma_1 + \gamma_2 (2\theta)$ and FWHM defined as $(U\tan^2\theta + V\tan\theta + W)^{1/2}$. The refinements also included 2θ zero-point correction and Chebyshev background parameters.

1 ($Bi_8[GaBr_4]_2$): An orthorhombic unit cell was indicated from the indexing of the reflections. Certain peaks could be attributed to bismuth metal impurities. On the basis of the similarities in the unit cell parameters of **1** with those of **3**, the compound was believed to be $Bi_8[GaBr_4]_2$. The Rietveld refinement was started with the structural parameters of **3**, including bismuth metal as a second phase. From the difference pattern it was observed that a third phase was present in the sample. The positions of the peaks for this phase matched the known positions of $GaBr_3$, which was included as a third phase in the refinement.[22] The final results suggested the ratio of the different phases in the sample to be Bi metal, 11.3(2)%; $GaBr_3$, 15.9(6)%; $Bi_8[GaBr_4]_2$, 72.8(1.1)%. The structural model of $Bi_8[GaBr_4]_2$ was refined using free coordinates for Bi_8 and restrained for $GaBr_4$ [Ga–Br = 2.35(1) Å]. Individiual isotropic thermal parameters were refined for Bi8 and one each for $GaBr_4$.

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-415130.

2 ($Bi_5[GaBr_4]_3$): The powder diffraction pattern was collected by using the MAXII synchrotron radiation source at Lund University (beamline I711, λ = 1.3700 Å), also equipped with an INEL CPS-120 detector. The wavelength was calibrated with a Si standard. The Rietveld refinement was started with parameters from cubic $Bi_5[GaCl_4]_3$. A different disorder pattern was found for the Bi_5^{3+} polycation, and the Bi positions were refined in general positions. The structural model was refined using free coordinates, coupled occupancies for Br sites, free for Bi. The thermal parameters were coupled for the Bi and Br sites respectively, and free for Ga (Table 5).

Table 5. Unit cell parameters and experimental crystal data of **1** and **2**.

Compound	$Bi_8[GaBr_4]_2$ (**1**)	$Bi_5[GaBr_4]_3$ (**2**)
Molecular mass ($g\,mol^{-1}$)	2450.51	2212.91
Crystal system	orthorhombic	cubic
Space group	$Pna2_1$ (no. 33)	Fm-$3c$ (no. 226)
a [Å]	18.3014(10)	17.6263(8)
b [Å]	10.3391(6)	
c [Å]	13.5763(7)	
V [Å^3]	2568.9(4)	5476.2(2)
Z	4	8
$D_{calcd.}$ ($g\,cm^{-3}$)	6.335	5.368
μ, [mm^{-1}]	112.54	71.79
Diffractometer	INEL CPS-120	INEL CPS-120
Radiation source	Cu-$K_{\alpha1}$	MAX II Synchrotron
Wavelength [Å]	1.540598	1.3700
Temperature, [K]	293	293
Scan range, 2θ [°]	8.0–108.0	11.0–100.0
Observations	3282	3039
Bragg reflections	1633	189
No. parameters refined	100	30
R_p	0.109	0.22
R_{wp}	0.114	0.26
R_b	0.069	0.099

Single-Crystal X-ray Diffraction: The crystal structure determinations of **3** and **4** were performed on a Bruker-Nonius KappaCCD diffractometer. Unit cell parameters and crystal data for **3** and **4**, respectively, are found in Table 6. **3** ($Sb_8[GaBr_4]_2$) crystallizes in the orthorhombic system, Laue group *mmm*. The systematic abscences led to the possible space groups $Pna2_1$ or *Pnma*, of which the former, non-centrosymmetric, space group was confirmed during the structure determination. **4** ($Te_4[Ga_2Br_7]_2$) crystallizes in the monoclinic system, Laue group 2/*m*. The space group $P2_1/c$ was indicated by the systematic absences. Because of the very weak intensities observed for reflections at high angles, the scan range was limited to 2θ = 50° for the data collection in the case of **4**.

All atoms were refined using anisotropic temperature parameters for both structures. Numerical absorption corrections were applied.[23] Both structures were solved and refined using direct methods and difference Fourier techniques using the SHELXS97/SHELXL97.[24,25]

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-415089 (for $Sb_8[GaBr_4]_2$) and CSD-415090 (for $Te_4[Ga_2Br_7]_2$), respectively.

Table 6. Unit cell parameters and experimental crystal data of **3** and **4**.

Compound	$Sb_8[GaBr_4]_2$ (**3**)	$Te_4[Ga_2Br_7]_2$ (**4**)
Molecular mass ($g\,mol^{-1}$)	1752.7	1907.9
Crystal system	orthorhombic	monoclinic
Space group	$Pna2_1$ (no. 33)	$P2_1/c$ (no. 14)
a [Å]	18.096(2)	10.1600(9)
b [Å]	10.1572(9)	10.8314(9)
c [Å]	13.2168(10)	13.8922(10)
β [°]		99.182(7)
V [$Å^3$]	2429.3(4)	1509.2(2)
Z	4	2
$D_{calcd.}$ ($g\,cm^{-3}$)	4.792	4.199
Crystal size [mm]	0.08 × 0.08 × 0.15	0.04 × 0.15 × 0.25
Temperature [K]	296	296
Radiation, λ [Å]	Mo-K_α, 0.71073	Mo-K_α, 0.71073
Monochromator	graphite	graphite
Data collection method	φ and ω scans	φ and ω scans
Scan range, 2θ [°]	9.02–55.00	9.26–50.04
Range in hkl	$-23 \le h \le 23$, $-11 \le k \le 13$, $-15 \le l \le 17$	$-13 \le h \le 11$ $-11 \le k \le 14$ $-17 \le l \le 18$
μ [mm^{-1}]	24.07	25.85
No. measured reflections	22945	15537
No. unique reflections	5077	2644
No. reflections, $I > 2\sigma(I)$	3411	2142
No. parameters refined	163	100
Max./min. Fourier peak [$e\cdot Å^{-3}$]	1.25/–1.20	1.17/–1.40
$R(\lvert F\rvert)$, all	0.103	0.068
$R(\lvert F\rvert)$, $I > 2\sigma(I)$	0.050	0.052
$wR(F^2)$, all	0.075	0.138
GOF	1.132	1.232
Flack parameter	0.00(2)	

The unit cell determination of Bi_6Br_7 was performed on a Siemens SMART P4 diffractometer.

Supporting Information (for details see the footnote on the first page of this article): Powder diffractograms, including final difference pattern, of **1** and **2**, Figures S1 and S2, respectively.

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